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OFFICE OF
PREVENTION, PESTICIDES
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MEMORANDUM **Date: 9/14/01**

SUBJECT: **Tier 1 Drinking Water Estimated Environmental Concentrations for propanil and its major degradate 3,4-dichloroaniline (3,4-DCA) from use on rice.**

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This memorandum transmits the estimated drinking water concentrations for Propanil and its major degradate 3,4-dichloroaniline (3,4-DCA) use on rice.

The Office of Pesticide Programs currently has no official model for estimating EECs in surface water for rice culture. Therefore a screening calculation method was developed and is provisional only. The SCI-GROW[1] model was used to estimate

groundwater concentrations for propanil and 3,4-DCA. Modeling results are shown in Table 1.

Table 1. Estimated environmental concentrations (ppb) of propanil and 3,4-DCA in surface and groundwater from use on rice.

Scenario	propanil		3,4-DCA		use(s) modeled	PCA
	peak	long term average	peak	long term average		
California	0.7	0.02	106	6.2	two applications on rice @ 4 lb ai/acre (1.3 lb ai/acre for 3,4-DCA)	Default PCA (0.87)
Gulf Coast	236	5.9	1007	59		
Mississippi Valley (overflow release)	489	12.2	1022	60		
Mississippi Valley (normal release)	0.65	0.02	118	6.9		
Groundwater/ (peak and long term average	#.001	#.001	0.354	0.354		

Estimates from the modeling are higher than the limited existing surface water monitoring data for propanil targeted to the pesticide use area.

Estimates from the SCI-GROW modeling do agree with limited existing groundwater monitoring data for propanil targeted to the pesticide use area.

Usage map for propanil[2] is attached.

Environmental Fate and Transport Assessment

Available data indicates that propanil will not persist in the field. Based on acceptable studies, propanil is rapidly metabolized under aerobic or anaerobic conditions in a water/sediment milieu (laboratory $t_{1/2}$ = 2-3 days). Acceptable aquatic field dissipation studies in rice paddies at two sites indicate short half-lives for propanil in the water (undetectable after no more than one day) and in the soil (sediment detections were near the quantitation limit, 0.01 ppm, by 2-7 days). The principle metabolic degradate, 3,4-DCA, reached a peak value (2.7 ppm) in soil (sediment) at 1 to 5 days after the second of two applications, remained high for 1 to 2 weeks, and was near detection limits, 0.01 ppm, for 4-6 months. Propanil is susceptible to biodegradation, yet stable to chemical degradative processes. Propanil metabolized rapidly in aerobic soil with a half-life of 0.5 days. However, propanil is stable to hydrolysis at pHs 5, 7, and 9 in the laboratory and, based on marginally acceptable study, propanil is stable to unsensitized aqueous photolysis. A supplemental soil photolysis study also suggests that propanil is stable to photodegradation, and the observed transformation was due mainly to metabolic activity.

The available mobility studies (K_{oc} values) indicate that propanil is in the medium mobility class for sand, sandy loam, and clay loam soils, and has low mobility in silty clay loam and silt loam soils (ASTM, 1996). The partition coefficient (K_d) for propanil ranges from 0.538 (sand) to 11 (clay loam), and K_{oc} values ranged from 306 (sand) to 800 (silt loam), respectively.

Acceptable aquatic field dissipation studies also indicate that propanil and 3,4-DCA are associated generally with the sediment rather than the aqueous phase. Detectable residues are confined largely to the top 2 inches of the sediment.

Based on mobility criteria detailed above (highly soluble, medium K_{oc} and K_d values), propanil could possibly reach groundwater but due to its rapid metabolism in a water/soil matrix, it is not likely to persist for a significant amount of time to leach in significant quantities. The possible exception are sites of extreme vulnerability and low metabolic capacity which would most probably occur only for terrestrial uses. If propanil does reach groundwater in these vulnerable areas, it is expected to be stable [in groundwater].

Surface Water

Monitoring

At the present time, the EFED has limited monitoring data on the concentrations of propanil and 3,4-DCA in surface water at the present time.

The USGS[3] reported in its pesticide occurrence and concentrations for for 62 agricultural streams sampled as part of NAWQA program (1992-1996), that propanil was detected in only 2.56% of the 1560 water samples analyzed with a maximum concentration of 2.05 ppb. The frequency of sampling and the length of sampling period were not enough to represent a good monitoring data to be used for a regulatory purposes.

3,4-DCA is a common degradate for diuron, linuron, and propanil. A USGS study analyzed 219 water samples collected in MS, MO, TN, AR, and North LA (mostly creeks, bayous and rivers) from February 1996-February 2001 (sampling every 2 weeks to one month) and showed that 3,4-DCA did not exceed 8.9 ppb in surface water (49 % detection rate, 68 samples). In South Louisiana, there were only three samples for 3,4-DCA[4], with a maximum concentration of 0.06 ppb. Any DCA present in MS, MO, TN, AR, and North LA is likely to be a result of both diuron and propanil applications due to both cotton and rice being produced. In South Louisiana, any 3,4-DCA present would most likely be from propanil applied to rice.

Modeling

Surface water concentration estimates were modeled for the three major rice growing regions in the United States, the Gulf Coast, California, and the Mississippi Valley including parts of northern Louisiana, Mississippi, Arkansas, and southern Missouri. A soil was selected for each region representative of those used for growing rice in that area. Agricultural management practices in each region and descriptions are provided in the table that follow to the extent they have been modeled in this assessment. The general management approaches to rice culture in each region are

summarized in Table 2. The sequence of events for modeling each region are in Table 3.

Table 2. Management Practices for Rice Growing Regions simulated[5].			
Management Practices	Gulf Coast	Mississippi	California
Seeding Method	Wet	Dry	Wet
Interval to Flood (Dry Seeded)	N/A	28 days	N/A
Flood Management Method	Pinpoint	Delayed	Continuous
Drain for Straight head Control	Yes	No	Yes

Table 3. Sequence of events for rice culture in each regional region scenario for surface water EECs.			
Day	Mississippi Valley	Gulf Coast	California
-7	Seeding		Seeding
0	Emergence	Seeding	Emergence
1		Drain Flood	
7		Flood	
12	1^{st} application	1^{st} Application	1^{st} Application
28	Flood		
33	2^{nd} application	2^{nd} Application	2^{nd} Application
36		Drain Flood	
43	Overflow release		Overflow release
90	Release Flood	Release Flood	Release Flood

The input parameters used in simulations are shown in Table 4.

Table 4.Chemical Properties and Application Practice Parameters Used to Estimate Environmental Concentrations from Rice use.			
Parameter	Value		Reference
	propanil	3,4-DCA	
Aerobic Soil Metabolism Half-life (d)	0.5 X 3	30 X 3	MRID# 41538701; Input parameters guidance[6].
Aerobic Aquatic Metabolism Half-life (d)	2 X 3	5 X 3	MRID# 41848701; Input parameters guidance.
Soil Water Partition Coefficient, K_d (L/Kg)	5.79	5.79	MRID# 42780401*; Input parameters guidance
Number of Applications	2	2	Product label (EPA Reg. No. 707-226)
Application Rate (lb ai/acre)	4	1.3/2.3**	Product label (EPA Reg. No. 707-226)
Application Interval	21 days	21 days	SMART Meeting (March 3, 2001)

*: The EFED has no K_{oc} data for 3,4-DCA, K_{oc} for propanil was used instead.
**: The maximum amount of 3,4-DCA formed from propanil is approximately 43.7 and 77 percent of propanil initially applied based on results from the aerobic soil metabolism study, and aerobic aquatic metabolism, respectively (MRID#41537801, MRID# 41848701). Therefore, a conservative application rate of 3,4-DCA was estimated based on the product of (1) the application rate of propanil; (2) the maximum conversion of propanil to 3,4-DCA (i.e., 0.437, 77); and (3) the molecular weight ratio of 3,4-DCA to propanil for mass balance on molar bases (i.e., 0.74).

Soils were chosen to represent those which are typical of rice culture in the Mississippi valley region. These soils are listed in Table 5. Properties for these soils used in modeling were taken from the STATSGO database[7]. Soil classification information was taken from the Soil Series description on the Internet[8].

Table 5. Soil and site properties for rice growing regions simulated[7].			
	Mississippi Valley	Gulf Coast	California
Soil Series	Sharkey	Evadale	Gridley
Soil Classification	Very-fine, smectitic, thermic Chromic Epiaquert	Fine, smectitic, thermic Typic Glossaqualf	Fine smectitic, thermic Typic Argixeroll
Bulk Density (kg L^{-1})	1.35	1.35	1.425
Organic Carbon Content (%)	1.30	0.725	1.16
Depth of Active Flooded Soil (cm)	1	1	1
Paddy Depth (cm)	10	10	10

The primary way that rice culture causes contamination of surface water with pesticides is through release of the flood water on the paddy. This can occur where precipitation causes overflow of the levee or through the intentional release of the paddy water as part of the agricultural management of the paddy.

The calculation described here attempts to estimate the concentration in the paddy water at the time of release as affected by soil and aquatic metabolism, and through binding to the paddy soil. The steps used to calculate EECs for Propanil are shown in Appendix I. The EECs for 3,4-DCA were calculated using the same method.

The expected drinking water concentration is based on the Index Reservoir in Shipman, Illinois. This is a 144,000 m^3 reservoir in a 172-hectare watershed. Based on the default Percent Cropped Area (PCA) factor of 0.87, we assumed that there would be a maximum of 150 hectares of rice paddies in the watershed. We assumed release of all 150,000 m^3 of paddy water into the reservoir on day 78 in California (i.e., normal release 90 days from planting), day 28 for the Gulf Coast (simulating a large storm 40 days after planting) and on day 43 in the Mississippi Valley, simulating a normal draining of the paddies

Groundwater

Monitoring

EFED has limited monitoring data on the concentrations of propanil in groundwater. Validated monitoring data for propanil for the states of California, Arkansas, Missouri, and Mississippi shows that propanil was detected only in two wells out of a total of 124 in Missouri. The range of concentration was 0.06 - 0.07 ppb[9].

In addition, the US Geological Survey (USGS) National Water Quality Assessment Program (NAWQA) analyzed pesticide occurrence and concentrations for major aquifers and shallow ground water in agricultural areas. Maximum propanil concentration in Samples (total 933) collected from major aquifers was 0.015 ppb (detection limit = 0.01 ppb). Maximum propanil concentration in 301 samples from shallow groundwater sites was 0.015 ppb[10], which is higher than that predicted using the SCI-GROW model.

The major component of the sampling design in the NAWQA study was to target specific watersheds and shallow ground water areas that are influenced primarily by a single dominant land use(agricultural or urban) that is important in the particular area. The ground-water data were primarily collected from a combination of production and monitoring wells. Groundwater sites in the ground-water data were sampled for pesticides from a single snap-shot in time.

Even though, the groundwater monitoring data collected by NAWQA are from sites considered as typical use areas, the frequency of sampling and the length of sampling period were not enough to represent a good monitoring data set to be used for regulatory purposes.

Modeling

The SCI-GROW model was used to estimate potential groundwater concentrations. SCI-GROW is a screening model for ground water. It is based on a regression approach which relates the concentrations found in ground water in Prospective Ground Water studies to aerobic soil metabolism rate and soil-water partitioning properties of the chemical. The input values are in Table 7 (see Appendix I for model output).

Input parameters used in SCI-GROW modeling of propanil and 3,4-DCA are shown in Tables 6, and 7, respectively.

Table 6. Ground Water Exposure Inputs for SCIGROW for Propanil.

MODEL INPUT VARIABLE	INPUT VALUE	Data Source
Application Rate (lbs. ai/A)	4 (rice)	Maximum use rate on product label
Maximum No. of Applications	2 (rice)	Maximum number of applications on the label
K_{oc} (ml/g)	239	Lowest non-sand K_{oc} was used (MRID 42780401)
Aerobic Soil Metabolic Half-life (days)	0.5	Half-life in sandy loam soil (MRID 41537801)

Table 7. Ground Water Exposure Inputs for SCIGROW for 3,4-DCA.

MODEL INPUT VARIABLE	INPUT VALUE	COMMENTS
Application Rate (lbs. ai/A)	1.3* (rice)	Maximum use rate on product label
Maximum No. of Applications	2 (rice)	Maximum number of applications on the label
K_{oc} (ml/g)	239 (propanil)	Lowest non-sand K_{oc} was used (MRID 42780401); Input parameters guidance[8].
Aerobic Soil Metabolic Half-life (days)	30	Half-life in sandy loam soil (MRID 41537801); Input parameters guidance.

*:**: The maximum amount of 3,4-DCA formed from propanil is approximately 43.7 percent of propanil initially applied based on results from the aerobic soil metabolism study (MRID #41537801). Therefore, a conservative application rate of 3,4-DCA was estimated based on the product of (1) the application rate of propanil; (2) the maximum conversion of propanil to 3,4-DCA (i.e., 0.437); and (3) the molecular weight ratio of 3,4-DCA to propanil for mass balance on molar bases (i.e., 0.74).

APPENDIX I

Propanil is to be applied to rice paddies no more than two times per year, at a maximum use rate of 4 lb ai/A/application. Applications are to be at least 21 days apart, and may be to dry or flooded paddies. The application is 4487 g/ha for both the first and second applications.

The Environmental Fate and Effects Division has no officially approved model to predict concentrations of pesticides in rice paddy water. The approach taken here was based on a hypothetical rice paddy, 1 hectare in size, flooded to a depth of 10 cm, with a sediment interaction zone of 1cm. Based on these dimensions, there are one million liters of water and 100 cubic meters of active sediment in the paddy. The sediment is assumed to weigh 135,000 kg based on a bulk density of 1.35 g/cc (Gulf Coast and Mississippi), and is assumed to weigh 142,500 kg based on a bulk density of 143 g/cc (California).

EEC Calculation for Propanil in Wet-Seeded Rice

The calculation steps for propanil EECs in wet-seeded rice paddies are as follows:

1) Calculate initial concentration (Ci) of chemical based on application rate and water volume in paddy.

$$Ci = 4487 \text{ g} \div 10^6 \text{ L} = 4.49 \text{ mg/L}$$

2) Calculate concentration in sediment (Cs) based on soil-water partition coefficient, Kd. Cs = Ci × Kd.
Silty clay loam Kd = 5.79 L/kg (MRID 42780401)

$$Cs = 5.79 \text{ L/kg} \times 4.49 \text{ mg/L} = 26.0 \text{ mg/kg}$$

3) Calculate mass of chemical in sediment (Ms) from Cs and mass of sediment. Ms = Cs × 135,000 kg.

$$Ms = 26.0 \text{ mg/kg} \times 135000 \text{ kg} = 3510 \text{ g}$$

4) Subtract mass of chemical in sediment (Ms) from initial mass of

chemical applied to paddy. Divide by volume of water in paddy to get concentration in water (Cw) on day 0.

$$Cw = (4487g - 3510\ g) \div 10^6\ L = 977\ \mu g/L$$

5) Calculate decay of chemical in paddy water according to first-order decay equation using aerobic aquatic metabolism half-life (2 days × 3 = 6 days; MRIDs 41848701, 41848601) as the rate constant, k. k = ln 2/2x3 = 0.116/day. Cw,t = (Cw,0) × exp(-0.116)(t). Repeat steps 1 to 5 for second application, and sum up resulting concentration for each day. Follow decay to 78 days (90 days from planting).

Table I-1. Results for Wet-Seeded Rice. (First application on day 0 is 2 weeks after seeding.)

Day	Application 1	Application 2	Sum (ppb)
0	977	—	977
1	870	—	870
4	614	—	614
10	306	—	306
21	85	977	1062
28	38	433	471 (peak Gulf Coast DW = 236 ppb)
56	1.5	17	18.5
78	0.11	1.3	1.4 (peak CA DW = 0.7 ppb)

EEC Calculation for Propanil in Dry-Seeded Rice

For dry seeded rice, the first application is assumed to be to dry paddies (1 cm of active sediment, 135000 kg), and the second application occurs 21 days later, and permanent flooding is on the 22nd day. The second application is degraded in the manner as for wet-seeded rice.

The chemical is decayed in soil with a half-life of 1.5 days (k = 1.04/day) for 21 days. The second application is on day 21 and is decayed at the aerobic aquatic rate, k = 0.116/day.

The calculation steps for propanil EECs in dry-seeded rice paddies are as follows:

1) Calculate concentration of chemical in soil (Cs) based on application rate and mass of soil (135,000 kg).

$$Cs = 4487 \text{ g} \div 135000 \text{ kg} = 33.24 \text{ mg/kg}$$

2) Decay chemical in soil according to aerobic soil metabolism rate (0.5 days × 3 = 1.5 days; MRID 41537801) as the rate constant, k. k = ln 2/1.5 = 1.04/day. Follow the decay to 21 days. Calculate the mass of chemical in soil left at 21 days from Cs at 21 days and the mass of soil. Partition this mass between the soil and the flood water.

3) Make the second application, and partition between water and sediment. Add the mass partitioning from the soil. Flood the paddy, and decay according to aerobic aquatic rate. Follow to 78 days (90 days from planting).

Table I-2. Results for Dry-Seeded Rice. (days 0-21 follow aerobic soil metabolism degradation rate, k = 1.04/day) (days 21-78 follow aerobic aquatic metabolism degradation rate, k = 0.116/day).			
Day	Application 1	Application 2	Sum
0	33.24	–	33.24 mg/kg
1	11.7	–	11.7 mg/kg
3	1.5	–	1.5 mg/kg
6	0.065	–	0.065 mg/kg
10	0	–	0
21	0	977	977 ppb (peak MS Valley DW = 489 ppb)
22	–	870	870 ppb
56	–	17	17 ppb
78	–	1.3	1.3 ppb (normal release DW = 0.65ppb)

Drinking Water Calculation

The expected drinking water concentration is based on the Index Reservoir in Shipman, Illinois. This is a 144,000 m^3 reservoir in a 172-hectare watershed. Based on the default Percent Cropped Area (PCA) factor of 0.87, we assumed that there would be a maximum of 150 hectares of rice paddies in the watershed. We assumed release of all 150,000 m^3 of paddy water into the reservoir on day 78 in California (i.e., normal release 90 days from planting), day 28 for the Gulf Coast (simulating a large storm 40 days after planting) and on day 43 in the Mississippi Valley, simulating a normal draining of the paddies.

The peak DW concentration is then the concentration of the paddy on the day of release divided by two, since the volume of the reservoir and the volume of the paddies are roughly equal. A chronic concentration was obtained by decaying the peak

concentration for a year at the aerobic aquatic rate, and taking the average over 365 days.

Application scenario

First application 4487 g/ha at 2 weeks after seeding or emergence.

Second application 4487 g/ha at a 21-day application interval.

For dry-seeded rice, permanent flood is 1 day after second application.

Release Scenario

California (wet-seeded): day 90 (78 days after first application, same as normal release time).

Gulf Coast (wet-seeded): day 40 (28 days after first application).

Mississippi Valley (dry-seeded): day 43 (10 days after second application).

SCI-GROW Output

```
SCIGROW Output for Propanil use on Rice


RUN No.   1 FOR propanil            INPUT VALUES
--------------------------------------------------------------------
    APPL (#/AC)  APPL.  URATE    SOIL    SOIL  AEROBIC
    RATE          NO. (#/AC/YR)  KOC   METABOLISM (DAYS)
--------------------------------------------------------------------
      4.000      2     8.000     239.0       0.5


   GROUND-WATER SCREENING CONCENTRATIONS IN PPB
-------------------------------------------------------
                     .00123
```

```
-------------------------------------------------------
  A=      .250  B=   244.000  C=     -.602  D=     2.387  RILP=    -1.437
  F=    -3.118  G=      .001  URATE=     8.000  GWSC=        .006100
```

SCIGROW Output for 3,4-DCA use on Rice

```
   RUN No.   1 FOR 3,4-DCA                 INPUT VALUES
--------------------------------------------------------------------
    APPL (#/AC)  APPL.  URATE    SOIL    SOIL  AEROBIC
    RATE          NO. (#/AC/YR)  KOC   METABOLISM (DAYS)
--------------------------------------------------------------------
      1.300      2       2.600   239.0     30.0

   GROUND-WATER SCREENING CONCENTRATIONS IN PPB
-------------------------------------------------------
                    0.354092
-------------------------------------------------------
  A=    85.000  B=   244.000  C=     1.929  D=     2.387  RILP=     3.111
  F=     -.343  G=      .454  URATE=     2.600  GWSC=       1.180124
```

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